

REMARKS

As to the drawing objection that requested drawings showing a septum and a Merlin valve, please consider that an example of septum is for instance shown in Fig. 2 of EP 0551847 (Grob et al. cited by the Examiner), and a Merlin valve is shown in the figures of US Patent No. 4954149 assigned to Merlin Instrument Company. The septum 1 is identified in Fig. 1 and identified as such on page 7 of the Specification, at line 17. Thus, the drawing objection is in error. Page 7, lines 19-20 mentions that the septum and Merlin valve are interchangeable. A new Fig. 3 is added to schematically identify a Merlin valve. As concerns depicting a coiled vaporization chamber, such is now represented by new Fig. 4. No new matter is added by this amendment.

The Specification was amended to address the objection to the disclosure. Entry is requested of the replacement sheets.

The Examiner rejects claims 1-5, 8, 9, 11, 13, 14, 15, 17 and 18 in his Official Action as being obvious in view of the teachings of Grob (EP 0551847) and Sasano et al. (US 6,203,597). The rejection is traversed.

To summarize briefly the inventive concept of the application:

The present application relates to a device and a method for vaporization injection into a gas chromatography analysis device.

The problem aimed to be solved by the present invention is to obtain more reliable quantitative analytical results by means of what is commonly called "classical splitless injection", which involves a permanently heated vaporization injector. In conventional splitless injection, the internal volume of the vaporizing chamber is scarce often insufficient, as it has to store the vapors of the sample until these are (slowly)

transferred into the column. The chamber is frequently overfilled, which results in loss of sample vapor by expansion backwards out of the chamber in the carrier gas supply line and the septum area. However, according to the known art, this internal volume can neither be enlarged by increasing the inner diameter for reasons of sample transfer into the column (the gas velocities become too low), nor by elongation since correspondingly longer needles are needed in order to release the sample close to the column entrance and fill the vaporization chamber from the bottom to the top (see the preamble of the specification).

A permanently heated vaporization injector is adapted for large volume samples and then having a large inner volume. This large inner volume cannot be obtained by increasing the injector inner diameter for reasons of sample losses, while, according to the known art, the length of the injector cannot be augmented at will due to the need of having correspondingly long needles (see the preamble of the specification).

This problem has been solved according to the present invention by exploiting the behavior of a liquid band released from the syringe needle when sample (solvent) evaporation inside the needle is suppressed; this liquid travels long distances through an empty hot tube as described in the specification (for instance see page 3, lines 8-15) and, thus, enables a release of the sample far away from the column entrance. This renders the technique more reliable and enables injection of larger volumes of sample. Hence:

- the vaporization chamber is elongated (to a length never before reached by conventional injectors)

- the syringe needle is short in order to almost totally avoid vaporization within the needle.

The sample and the solvent are injected into the upper portion of the vaporization chamber. Due to suppression of sample evaporation in the needle, the sample liquid forms a band moving at high velocity about 10 m/s) through the vaporization chamber. During this short time, evaporation remains negligible (time-consuming heat transfer). The liquid does not contact the hot liner walls because the vapors formed upon approaching the hot surface repel the liquid and redirect the band towards the bottom of the injector. Due to its high velocity and the repulsion from hot surfaces, the band of liquid may travel over long distances, even if the chamber is curved (see the specification on page 7, lines 19-27). This is the heart of the invention as it enables one to elongate the injector chamber without elongating the syringe needle (in fact the needle is shortened). The liquid sample is transferred onto a stopping material (packing) or trapped between obstacles positioned just above the column entrance (page 10 lines 8-12), which is the center of sample evaporation. Thus, the whole sample is transferred onto the column in evaporated form.

✓ Please note that the vaporization chamber is permanently heated (likewise to the cited Grob et al. document which is the closest prior art). The whole injector is at temperatures above the solvent boiling point, but there is a gradient from the region around the column entrance kept at the set temperatures to a lower temperatures towards to septum (see the specification page 3, lines 25-28 in combination with page 11, lines 22-28), which is true for all permanently heated injectors on the market. The vaporization of the sample (primarily the solvent) within the needle is almost completely

prevented by using a short needle (small thermal capacity) only reaching a moderately heated zone. Claim 1 recites that the vaporization within the needle is negligible (see the specification at page 5 last line).

The vaporization of the sample and the solvent within the needle is prevented by using a short needle. Accordingly, the sample and solvent are introduced into the upper portion of the vaporization chamber in form of a liquid band. Due to the fact that small quantities of solvent vaporize on the wall of the chamber, the sample and the remaining solvent travel in a practically unaltered form (liquid band) a far distance across the chamber without touching the chamber walls (see the specification on page 7, lines 19-27). That is why the chamber may have also a coiled geometrical shape because the liquid band "slits" on the small solvent layer vaporized on the chamber wall and it freely follows the geometrical shape of the chamber. For the same reason, the gas-chromatographic analysis is facilitated in the case of samples having large volumes, since the chamber volume may be increased by means of increasing its length.

In contrast to the present invention, the known gas-chromatographic analytical devices with vaporization chamber needles long enough for injecting the sample into the lower portion of the chamber, near to the analytical column in order to avoid sample loss occurring towards the top of the chamber and such long needles may become bent when introduced through the septum. Furthermore, the sample should be introduced in a very short period of time, which is a very critical operation when the injection is carried out manually. A long needle requires several attempts to be introduced into the chamber and thus the sample and solvent may partly vaporize within the needle.

Therefore, the injection with a long needle can be carried out only by using automatic samplers in order to reduce the discrimination phenomenon of the sample.

Furthermore, if a sample having a large volume is injected into the lower portion of the chamber, the chamber volume can be increased by means of increasing the diameter (width) of the chamber, which, however, leads to sample loss (the low carrier gas flow hardly transfer the samples vapors into the column if the chamber is excessively large). Therefore, in contrast to the state of the art, the device and method according to the present invention allows a reliable analysis also of samples having large volume and also in case of manual sample injection, without any need to eliminate the solvent vapors before the sample transfer into the column.

According to one of the preferred embodiments of the present invention the lower portion of the vaporization chamber is heated to a temperature sufficient to vaporize all the sample while the parts above this zone are heated to a temperature which avoids an excessive heating of the needle allowing the introduction of the sample in liquid band. Therefore, two new Claims 19 and 20 are added that incorporate this subject matter (underlined) and depend on both the existing device claims and on the existing method claims. This subject matter is set forth in the specification (see page 11, lines 22-28, page 7, lines 7-9 and lines 18-20 and Fig. 1), thus their introduction in new claims is supported by the originally filed specification.

Claims 1-5, 8, 9, 11, 14, 14, 15, 17 and 18 were rejected under 35 USC § 103 over Grob (EP 0551347) in view of Sasano et al. (US 6,203,597). This rejection is traversed.

Grob t al. (EP-A-0551847) disclose a device for vaporization injection of large volumes of samples in what is commonly called the "overflow" mode: solvent vapors are intended to flow backwards out to the injector and exit through the widely opened septum purge outlet. This technique enables injection of extremely large volumes into rather small chambers, but there is escape of volatile sample material together with the solvent vapor. No temperature variation in the vaporization system is required and the sample injection is carried out at high temperatures (see column 2, lines 50-57).

Accordingly, the sample is injected into a vaporization chamber heated at a temperature that exceeds the boiling point of the sample solvent and is equivalent or higher than the temperature necessary for transferring to the column also the most high-boiling compound present in the sample (see column 6, line 36-46). In order to house the sample in the hot chamber, a cool zone, having the temperature corresponding to the boiling point of the solvent, is formed by means of introducing an exhaustible cold source into the vaporization chamber or by means of inert materials having a low thermal mass. The injected sample solvent vaporizes on said inert materials and cools the latter to the solvent boiling point (see column 3, lines 35-56). Since the temperature of the vaporization chamber is above the boiling point of the solvent, the end of the needle must be positioned in such a manner that the sample reaches the inert material still in liquid condition in order to avoid sample evaporation from the needle tip or in the gas phase and consequently sample loss with the solvent vapors leaving the vaporization chamber through duct 6 (see column 7, lines 7-22). This system allows the injection of large volume samples due to the fact that the solvent vapor is vented, not by enlarging the chamber as in the present invention. However, venting of the solvents

limits the compounds that can be analyzed to non-volatiles (volatile compounds are lost with the solvent vapors).

It is evident that the syringe needle should arrive near to the cooled zone (by using e.g. inert materials), namely into the lower part of the vaporization chamber in order to obtain that sample reaches the inert material still in liquid condition within the vaporization chamber having high temperature (see column 7, lines 17-26).

In contrast, the present invention avoids overflow (and the loss of volatile sample components) i.e., expansion of vapors backwards out of the injector. It can afford to do so because of the enlarged volume of the chamber. As an additional difference, the technique described in EP-A-0551847 presupposes a long syringe needle depositing the sample near the bottom of the chamber, with all the inconveniences related to this. The sample liquid does not travel as a band over a long distance through empty heated tube, but is introduced into packing material located at the needle tip.

Sasano et al. (US 6,203,597) disclose an apparatus and a method for mass injection of a sample by a PTV technique, i.e., starting with a low initial temperature. In contrast, the present invention concerns an improvement of what is commonly called "classical splitless injection", while the patent US 6,203,597 is related to Programmed Temperatures Vaporizing (PTV) injection. The two techniques are fundamentally different and involve correspondingly different injectors. The former technique involves an injector kept at a constantly high temperature, adjusted to the evaporation of the sample components. The latter applies a low initial injector temperature, i.e., a temperature below the solvent boiling point. Usually at the end of solvent evaporation, the temperature is increased to a level permitting evaporation of the solutes. The two

techniques differ in many respects. One of the inherent drawbacks of the classical splitless injection is that the whole volume of solvent vapor must be stored in the vaporizing chamber for the time until it is transferred into the column, which requires the large volume of the injector chamber and is the reason why the elongated chamber of this application is such an important advantage. PTV injection does not need to store the solvent vapors since these are formed slowly, i.e., concurrently with the transfer into the column.

The vaporization chamber is provided with a liner (6) having a temperature lower than the boiling point of the sample solvent (see column 4, lines 2-4). An oven is installed at the bottom of the vaporization chamber (1) around the column (see column 3, lines 8-9 and column 4, lines 45-46). The temperature of the oven (10) is higher than the boiling point of the solvent in order to prevent the solvent from flowing into the pre-column (see column 4, lines 5-8). The sample is injected into the liner in a conventional manner (see column 4, lines 1-2) which means an injection into the central portion or lower portion of the vaporization chamber. The liner (6) has a tapered narrow portion (64) toward the column (9) wherein a resistance member (65) (glass bead) may be placed (see Fig. 4 and column 3, lines 26-30). In the vaporization chamber, there is a constant evaporation of the solvent and the resulting solvent vapor is removed through the split purge (5) (see column 4, lines 57-61).

The liquid sample is kept in place by a glass bead (65).

✓ Note even the combination of the teachings of Grob et al. and Sasano et al. leads to the subject matter of the amended claims 1 and 17.

This invention relates to an injector in which the sample is injected into a permanently hot chamber but maintains its liquid state up to the stop means, allowing the construction of chambers having a length greater than the limits of previous injectors. The Examiner's assertion that *"it is well within the purview of the skilled artisan to vary the placement of the stop to achieve various results with the injection rate"* is not true according to what state in the specification with reference to the chamber sizes.

Sasano et al. do not teach or suggest the injection of the sample into the upper portion of the vaporization chamber by using short needle. In fact, Sasano et al. teach a sample injection carried out in a conventional manner, namely into the lower portion of the vaporization chamber, and the use of a vaporization chamber having a temperature lower than the boiling point of the sample solvent rather than a vaporization chamber heated or partially heated according to the amended claims 1 and 17.

Sasano et al. do not teach or suggest to enlarge the vaporization chamber in order to permit large sample volume introduction. In fact, Sasano et al. realize large volume injection by eliminating the solvent vapors before transferring the sample into the column. As in the application of Grob et al. (EP-A-05518470 the solvent elimination unavoidably leads to loss of the most volatile components restricting the technique to the analysis of semi-volatile or non-volatile substances. Additionally, this system requires a vaporizing chamber that must be temperature programmed adding complexity to the method set up.

The combination of the teachings of Grob et al. and Sasano et al. does not lead to the subject matter of the amended claims 1 and 17.

In summary, Grob et al. relates to an injector wherein the injected sample vaporizes immediately at the needle exit, and then the solvent vapors are separated and vented. Sasano et al. relates to an injector in which the sample is introduced in liquid state in a cool chamber.

The invention relates to an injector in which the sample is injected in a hot chamber but maintains its liquid state up to the stop means, allowing the construction of chambers having a length greater than the limits of previous injectors.

The Examiner's assertion that *"it is well within the purview of the skilled artisan to vary the placement of the stop to achieve various results with the injection rate"* is not true according to what stated in the specification with reference to the chamber sizes.

In view of what is set forth hereinabove, it is evident that the subject matter of claims 1 and 17 are novel and unobvious over Grob et al. and Sansano et al. Consequently, also the claims depending on said independent claims are novel and unobvious.

Enclosed is a Petition for a one month extension of time along with a Petition fee in the amount of \$55.00 (37 CFR 1.17(a)). The Commissioner is authorized to charge any deficiency or to credit any overpayment to Deposit Account 03-3839.

Dated: April 4, 2003

Respectfully submitted,



Robert J. Hess

Reg. No. 32,139

GIBBONS, DEL DEO, DOLAN
GRIFFINGER & VECCHIONE
One Pennsylvania Plaza - 37th Floor
New York, NY 10119-3701
Tel (212) 649-4700
Fax (212) 333-5980